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Preparation and Characterization of Alumina based TiN_n and SiC_n Composites

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ABSTRACT

Ceramic composites containing 2 and 5 vol. % of nanosized commercially available TiN and SiC particles in alumina were prepared via a water based slurry processing route followed by spark plasma sintering (SPS) at 75 MPa in the temperature range 1200-1600°C. Some of the samples could be fully densified by use of SPS already after five minutes at 1200°C and 75 MPa. The aim was to control the alumina grain growth and thus obtain different nano-structure types. The microstructures have been correlated to some mechanical properties; *e.g.* hardness and fracture toughness.

INTRODUCTION

The weakest link in a chain determines the strength. This is an expression, which is applicable to most areas within the subject of materials science. It becomes especially obvious in the case of ceramics since these materials exhibit a brittle behaviour. In order to obtain improved toughness of ceramics one have to find ways to make the material homogeneous and free from cracks, pores and inclusions. Except for these fundamental but also unattainable details introducing reinforcement material in the matrix can also increase the toughness. Particles of a second phase in a matrix can act as reinforcement by different toughening mechanisms depending on *e.g.* composition, particle size, powder-processing route and thermal expansion properties.

Nano-sized particles have higher intrinsic sintering activities than micron sized ones and therefore a lower sintering temperature is expected to be required when sintering such particles. Nano-composites have proved to exhibit very good mechanical properties, with new toughening mechanisms. During the last decade an increasing interest for the nano sized region have been raised. Niihara and co-workers managed in the early 90'ies to obtain nano-sized particles embedded in or in-between larger alumina grains [1]. The mechanical properties were outstanding, but the results have been difficult to reproduce for other research groups.

Both TiN and SiC are used in construction ceramics as reinforcement of alumina. However, since the thermal expansion are different; TiN having a higher, and SiC having a lower thermal expansion than that of alumina, the expected properties should be different. For instance, at room temperature after sintering, in the case of SiC/alumina composites, the SiC particles are compressed and the matrix is tensile stressed. The conversed scenario is expected for TiN/alumina. But, however, that implies strong inter granular bonds between TiN and alumina. Therefore the surface properties *e.g.* the degree of surface oxidation or impurities plays important roles for the internal stress fields and therefore mechanical properties. This ought to be especially crucial for nano composites since the grain boundaries become more and more prominent when the particle size reduces.

The aim of this project was to obtain homogeneous powder mixtures with 2 vol.% and 5 vol.% nano-sized TiN and SiC particles dispersed in fine-grained alumina, to sinter them fully densified with spark plasma sintering (SPS) and to correlate the microstructures to mechanical properties. By applying different sintering parameters, in this case the temperature, attempts to tailor the microstructure were planned.

Alumina reinforced with TiN or SiC nano particles have been extensively reported earlier *e.g.* [1-3], but not this processing route. It was shown in a former investigation [3] that an admixture of 10 vol.% of TiN nano particles in alumina was too much in order to have the particles separated, while 5 vol.% seemed to be suitable. In the present study we added 5 vol.% of nanoparticles but also investigated the effect of a further decrease (to 2 vol.%) in the nanoparticle admixture. Measurements on zeta potentials on similar ceramic powders have shown that the pH_{iep} is about 3-5 for TiN [3-5], and 2.5-3 for SiC [6] whereas it is about 9 for Al_2O_3 [3,6]. However when adding a small amount (0.5 wt.%) of a poly acrylic acid (PAA) dispersant to an alumina/water suspension the pH_{iep} is decreased to about 3 and furthermore the dispersant yields a pH of about 9. This means that well dispersed low viscous composite slurries can be obtained without further controlling the pH. This behaviour was utilized for the preparation of both TiN and SiC composites.

EXPERIMENTAL

The powders used in this study are given in table I. The powder morphologies were studied at 200kV in a TEM (Jeol, 2000FX, Japan). The samples were prepared by putting droplets of powder/ethanol suspensions onto copper grids and letting the ethanol evaporate (figure 1 a-c). Due to the small size and the dry state of samples, the particles tend to form agglomerates, which are deagglomerated during the processing.

The nano sized TiN powder is pyrogenic and was therefore handled in a glove box under nitrogen and suspended in ethanol-water mixture to obtain a slow surface oxidation. Then the solvent was evaporated at 50°C so that the powder could be handled in air. The SiC nanoparticles were suspended directly into alumina/water slurries according to the following powder processing scheme (figure 2).

Table I. The powders used in this investigation.

	TiN _{nano}	β-SiC _{nano}	α-Al ₂ O ₃
Manufacturer	H. C. Starck (Germany)	MTI Corporation (U.S.A)	Taimci Chemicals Co. Ltd (Japan)
Powder Grade	Nano TiN	Nano β-SiC	Taimicron TM DAR
Particle size (nm)	30 (BET equivalent spherical diameter)	30	100
Purity (%)	*	95	99.99

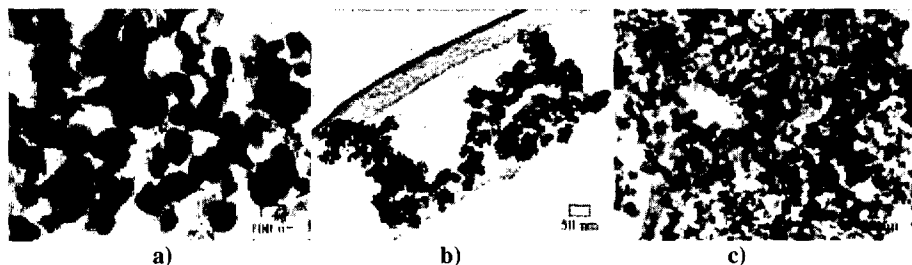


Figure 1 a-c. TEM images showing the powders used in this investigation; a) Al_2O_3 b) TiN and c) SiC.

Alumina powder, deionised water, and 0.5wt. % of poly acrylic acid (Dispex A40, Allied Colloids, USA) were mixed for 30 minutes at 400 rpm in a planetary ball mill (Pulverizette 6, Fritsch GmbH, Germany) equipped with a 250ml SiAlON milling jar and SiAlON milling spheres. Then 2 vol.% and 5 vol.% of the reinforcement phases were added and the slurries were milled for another 10 minutes. After equilibration the slurries were freeze granulated by spraying the slurry through a nozzle into liquid nitrogen. The granules were finally freeze dried in a freeze dryer (Hetosicc, Heto-Holten A/S, Denmark).

According to the former investigation [3] we could obtain homogeneous composites without additions of grain growth inhibitors like MgO and sintering in a hot press furnace. In the present investigation a finer alumina powder was used and the powder mixtures were sintered in another manner. In the sintering experiments of this investigation the dry powder mixture was poured directly into a graphite dye, which were put in the Spark plasma-sintering (SPS, Dr. Sinter, Japan) device. The heat increment in the SPS was maintained by using a pulsed DC according to figure 3a. A typical sintering cycle is represented in figure 3b.

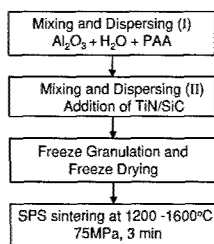


Figure 2. Processing scheme for the composite preparation.

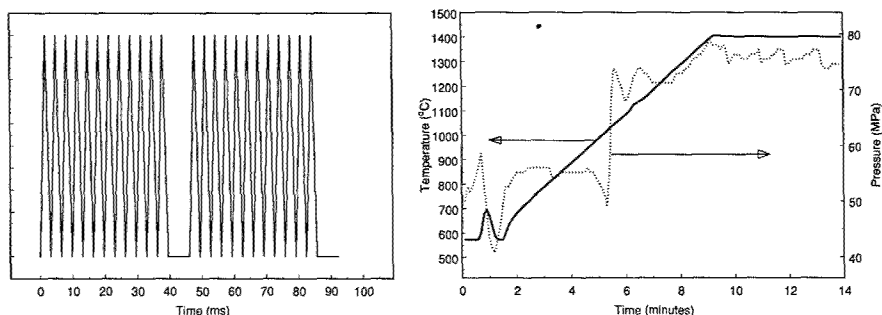


Figure 3. a) Schematic illustration showing the used SPS pulse duration for the sintering experiments. b) Temperature and pressure profiles for a typical SPS sintering cycle.

The samples were exposed to 1200, 1400 and 1600°C with the pressure 75MPa for 5 minutes. The densities of the sintered samples were measured by Archimedes principle using tap water. The theoretical density of the composites were calculated assuming a density of 3.97g*cm⁻³ for Al₂O₃, 3.22g*cm⁻³ for SiC, and 5.21g*cm⁻³ for TiN. For mechanical measurements pieces were

polished and the Vickers hardness were measured using a square based diamond for indents with an indenter using the load 5kg parallel to the pressing direction. The Vickers hardness was calculated using the expression (2):

$$H=1.8544 \cdot P/a^2 \tag{2}$$

Where P is the load in Newton and a is the length in metres of the diagonal of the obtained indentation.

The mode I fracture toughness was determined measuring the lengths of the yielded cracks according to [7](3):

$$K_{IC}=A \cdot (E/H)^{1/2} (P/C^{3/2}) \tag{3}$$

Here, A is a constant and was set to 0.016, C is the mean crack length (meter), H is the hardness from (1), P is the load (Newton) and E is the Young's modulus which was assumed to have a constant value of 390GPa for all composites. This is consistent with values of a similar investigation [8].

In order to reveal the microstructure of the samples fracture surfaces were prepared by crushing the composites. The samples were put onto a conductive tape and investigated in a FEG SEM (Leo 1550, Germany) at 10kV (without any additional sputtered conductive layer) and a SEM (Jeol, 880, Japan) at 20kV (with a sputtered layer of gold).

RESULTS AND DISCUSSION

After sintering it was found that the SiC composites required at least 1400°C for densification while the TiN nano-composites could be almost fully densified already after sintering at 1200°C (table II). But, however the 5 vol. % TiN composite exhibited a lower density at 1600°C. The explanation to this may be found in the PAA additions. The dispersant was not burnt off before sintering and at least two different scenarios could be considered; There could be carbon containing remnants at the grain boundaries which in contact with surface oxides produces CO(g) which then could be trapped in the structure because of the rapid sintering cycle. The other scenario is that gaseous decomposition products from the dispersant itself is trapped in the matrix. However, this does not explain why the SiC composites do not show the similar behaviour. The actual reason remains to be solved.

Table II. Percent of theoretical density, hardness, and fracture toughness.

Composite	1200°C			1400°C			1600°C		
	%ρ _{th}	H _{V5} (GPa)	K _{IC} (MPam ^{1/2})	%ρ _{th}	H _{V5} (GPa)	K _{IC} (MPam ^{1/2})	%ρ _{th}	H _{V5} (GPa)	K _{IC} (MPam ^{1/2})
2vol.% TiN	99.9	20.3	3.7	98.9	16.7	3.8	99.0	15.5	*
5vol.% TiN	98.7	20.7	3.2	97.9	17.0	3.4	96.2	13.9	4.1
2vol.% SiC	92.5	(15.2)	(3.5)	99.4	20.6	2.8	99.9	19.3	2.8
5vol.% SiC	89.8	(11.5)	(3.9)	97.4	19.8	3.0	99.4	19.8	2.5

*Immeasurable cracks. Values in brackets are misleading because the samples are not fully dense.

As the sintering temperature increases the (alumina) grains are expected to grow (especially without additions of MgO). This was also found in the present investigation and is obvious in the fracture surface images for e.g. the 2 vol.% TiN and SiC composites (figures 4 a-c and 5 a-c). The resolution of the FEG SEM is high enough to reveal the nanoparticles in the 1200°C composite. It is evident in fig 4a that the alumina grains have grown somewhat already after the short sintering at 1200°C and some nano particles seem to be within the alumina grains. The rapid heating by means of SPS sintering involves very high electric currents through the material. This enhances surface diffusion and could also lead to closed porosity. As the temperature increase also the nanoparticles grow to agglomerates (figure 4b-c). This is also reflected in the mechanical behaviour. Both the hardness and fracture toughness tend to decrease with increasing sintering temperature (table II). It is evident from figures 4 and 5 that SiC composites show more transgranular fracture surface features than the TiN_n composites and they exhibit SiC agglomerates implying a less homogeneous powder mixture. The reason for this is not clear. Generally, the SiC composites are harder but have somewhat lower fracture toughness than TiN composites. It should be noted that these data are not to be considered as absolute values, but rather as a base for internal comparison. However, from these results it could be concluded that low sintering temperature is desirable, but the reinforcement admixture (2 or 5 vol %) is less important. For the TiN composites sintered at higher temperatures a strange indent behaviour showed up which involved absence of sharp indent profiles. A plausible explanation to this phenomenon could be found in the larger thermal expansion difference at elevated temperatures giving rise to stress fields in the material, which is released during the indentations but also in probable closed porosity.

A subsequent annealing of the compacts after sintering has been suggested for improving the mechanical behaviour by ordering of dislocation structures [1,9]. The role of such annealing has not been investigated in this study.

CONCLUSIONS

Fully densified nano composites comprising alumina and well dispersed nanoparticles of TiN or SiC could be obtained using a water based processing scheme followed by SPS sintering at 75MPa. The TiN composites sintered already at 1200°C whereas the SiC composites required higher temperatures. An unexpected drop in density for the TiN composites sintered at higher temperature is not yet explained.

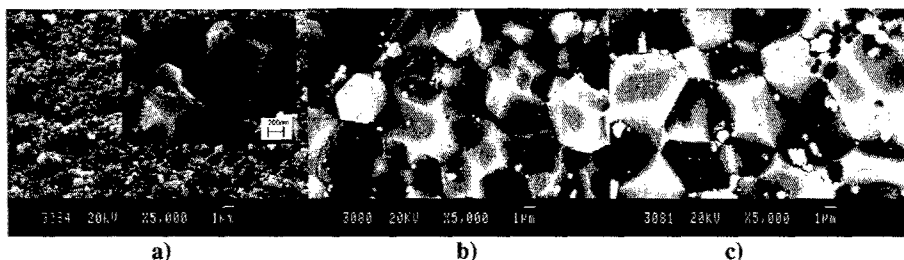


Figure 4a-c. BSE SEM images showing fracture surfaces of 2 vol.% TiN/Al₂O₃ composites sintered at 75 MPa for 5 minutes at **a)** 1200°C (where the microstructure is revealed by the FEG SEM inset) **b)** 1400°C, and **c)** 1600°C. Note the substantial temperature dependent grain growth of alumina (dark grains) and agglomeration of TiN particles at 1400°C and higher (lighter spots).

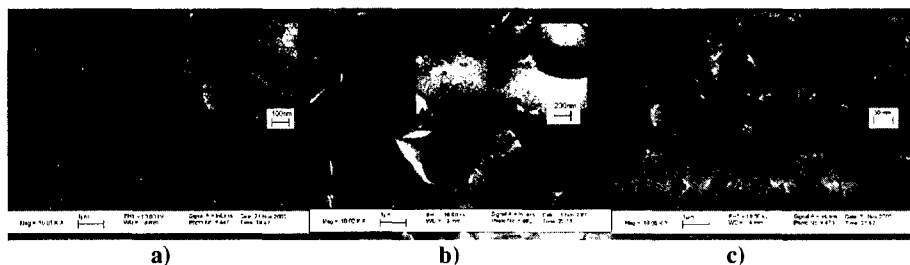


Figure 5a-c. FEG SEM images with magnified insets showing fracture surfaces of 2 vol.% SiC/Al₂O₃ composites sintered at 75 MPa for 5 minutes at **a)** 1200°C, **b)** 1400°C, and **c)** 1600°C. These composites show more of transgranular fracture surfaces than the TiN_n composites and the SiC_n particles are less homogeneous dispersed than TiN_n composites.

Measurements of hardness and fracture toughness showed that the lowest possible sintering temperatures are desirable from mechanical properties point of view. No great differences between 2vol% and 5vol % composites could be observed for either TiN- or SiC-composites. When fully dense, the SiC composites were harder than TiN composites, but had somewhat lower fracture toughness. The measurements were hard to perform on some of the composites because a strange behaviour of the indents, probably depending on stress fields in the composites.

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